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(21) International Application Number: PCT/US99/03006 (22) International Filing Date: 12 February 1999 (12.02.99) (30) Priority Data: 60/074,722 13 February 1998 (13.02.98) US (71) Applicant (for all designated States except US): EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; P.O. Box 390, 180 Park Avenue, Florham Park, NJ 07932-0390 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MURPHY, William, John [CA/US]; 16445 Coliseum Avenue, Baton Rouge, LA 70816 (US). CODY, Ian, Alfred [CA/US]; 7942C Wrenwood Boulevard, Baton Rouge, LA 70809 (US). WITTENBRINK, Robert, Jay [US/US]; 836 Shadyglen Drive, Baton Rouge, LA 70816 (US). SOLED, Stuart, Leon [US/US]; 21 Cooks Cross Road, Pittstown, NJ 08867 (US). McVICKER, Gary, Brice [US/US]; 65 Main Street, Califon, NJ 07830 (US). HANTZER, Sylvain [FR/US]; 37620 Seven Oaks Avenue, Prairieville, LA 70769 (US). LINEK, Sandra, Jean [CA/US]; 5202 Claycut Road, Baton Rouge, LA 70806 (US).		(74) Agents: SCUORZO, Linda, M. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (81) Designated States: AU, CA, JP, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR IMPROVING BASESTOCK LOW TEMPERATURE PERFORMANCE USING A COMBINATION CATALYST SYSTEM (57) Abstract Waxy feeds are converted to a basestock using a unitized mixed powdered pellet catalyst comprising a metal hydrogenation component on a support having a first dewaxing component and a second isomerization component, wherein the first component is selected from 10 and 12 ring molecular sieves and mixtures thereof and the second component is an amorphous inorganic oxide. The first and second components are present in a ratio sufficient to promote wax isomerization and naphthene distractions without substantial decrease in VI.		

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PROCESS FOR IMPROVING BASESTOCK LOW TEMPERATURE PERFORMANCE USING A COMBINATION CATALYST SYSTEM

FIELD OF THE INVENTION

This invention relates to the hydrodewaxing of waxy feeds including slack wax, slack wax isomerate, Fischer-Tropsch wax, Fischer-Tropsch hydroisomerate, waxy raffinates, and waxy distillates to produce a lube oil basestock or blending stock. More specifically, this invention relates to the conversion of a waxy feed using a mixed catalyst capable of promoting wax isomerization and naphthene destruction to form a lube basestock with minimum VI loss and having good low temperature properties.

BACKGROUND OF THE INVENTION

The performance criteria for lubricants such as those used in automatic transmission fluids and passenger car engine oils has become increasingly more severe with users requiring basestock that provide better wear protection, improved volatility and low temperature properties.

Waxy feeds can be converted to liquid products using well known catalytic dewaxing catalysts; however, in these instances the selective cracking of paraffins typically results in a loss of viscosity index (VI) which is undesirable.

In contrast, isomerization of waxy feeds using molecular sieve based catalyst that have linear 1D pore structures produces lube basestocks without loss in VI. While this isomerization process offers benefits over that of catalytic dewaxing there nonetheless remains a need for different and improved

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processes for converting waxy feeds to lube basestocks without significant loss in VI and which basestock has good low temperature properties.

SUMMARY OF THE INVENTION

This invention relates to a method for the hydrodewaxing of feeds to produce a lube basestock having improved low temperature properties which comprises: contacting the feed with a unitized mixed powder pellet catalyst under hydrodewaxing conditions, the catalyst comprising a metal hydrogenation component on a support having a first dewaxing component and a second isomerization component, wherein the first component is selected from 10 and 12 ring molecular sieves and mixtures thereof and the second component is an amorphous inorganic oxide and wherein the first and second components are present in a ratio such that when evaluated in the conversion of methyl cyclohexane at 320°C to 1,1-dimethylcyclopentane, 1,2-dimethylcyclopentane, 1,3-dimethylcyclopentane and ethylcyclopentane, the catalyst will provide a trans-1,2-/trans-1,3-dimethylcyclopentane in the range of at least 1, and a selectivity to ethylcyclopentane, at 10% conversion, of at least about 50%.

This and other embodiments of the invention will be discussed below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing showing the conversion of methylcyclohexane to various cyclopentane compounds at 320°C.

Figure 2 is a graph showing Brookfield viscosity vs. yield for various catalyst mixtures.

DESCRIPTION OF THE INVENTION

The feed suitable in the practice of the present invention includes waxy hydrocarbon oils such as slack wax, slack wax isomerate, Fischer-Tropsch wax, Fischer-Tropsch hydroisomerate, waxy raffinates and waxy distillates. Typically, such feeds will have wax contents of 15% or more. The preferred feed will have a nitrogen and sulfur content each below about 20 wppm by weight. Indeed, if the feed contains higher amounts of sulfur and nitrogen, the feed can be first subjected to hydrotreating under typical hydrotreating conditions to reduce the sulfur and nitrogen contents. Any of the conventional hydrotreating catalysts can be employed like Ni/Mo on alumina, Ni/W on alumina Co/Mo on alumina. In other words any of the Group VIB to Group VIII and mixtures thereof (the metal groups referred to here and hereinafter are those metals of the Periodic Table of Elements; Sargent-Welch Scientific Co.) on metal oxide refractory supports may be employed. Commercial examples of such are identified as HDN-30 and KF-840.

Hydrotreating is conducted so as to lower the sulfur and nitrogen contents to levels of 20 ppm or less nitrogen or 20 ppm or less sulfur especially 10 ppm less nitrogen and 10 ppm or less sulfur and most preferably to levels below 5 ppm for nitrogen and 5 ppm or less for sulfur.

Waxy feeds secured from natural petroleum sources contain quantities of sulfur and nitrogen compounds which are known to deactivate wax hydroisomerization catalysts. To prevent this deactivation it is preferred that the feed contain no more than 10 ppm sulfur, preferably less than 2 ppm sulfur and no more than 2 ppm nitrogen, preferably less than 1 ppm nitrogen.

To achieve these limits the feed is preferably hydrotreated to reduce the sulfur and nitrogen content.

Hydrotreating can be conducted using any typical hydrotreating catalyst such as Ni/Mo on alumina, Co/Mo on alumina, Co/Ni/Mo on alumina, e.g., KF-840, KF-843, HDN-30, HDN-60, Criteria C-411, etc. Similarly, bulk catalysts comprising Ni/Mn/Mo or Cr/Ni/Mo sulfides as described in U.S. Patent 5,122,258 can be used.

Hydrotreating is performed at temperatures in the range 280°C to 400°C, preferably 340°C to 380°C at pressures in the range 500 to 3000 psi, hydrogen treat gas rate in the range of 500 to 5000 SCF/bbl and a flow velocity in the range 0.1 to 5 LHSV, preferably 1 to 2 LHSV.

The hydrotreated waxy oil is stripped to remove ammonia and H₂S and then is subjected to the hydrodewaxing process of the present invention.

The catalyst employed in the hydrodewaxing of waxy feeds in accordance with the present invention is a unitized mixed powdered pellet catalyst. The term "unitized" as used here and in the claims means that each pellet is one made by mixing together a powdered first catalytic component with a powdered second catalytic component and pelletizing the mixture to produce pellets each of which contain all of the powder components previously recited.

The unitized catalyst can be prepared by starting with individual finished catalysts, pulverizing and powdering such individual finished catalysts, mixing the powdered materials together to form a homogeneous mass, then compressing/extruding and pelleting thus producing the unitized pellet catalysts comprising a mixture of the individual, different, and distinct catalyst

components. Pulverizing and powdering is to a consistency achievable using a mortar and pestle or other such conventional powdering means.

The catalyst used in the process of the present invention comprises a metal hydrogenation component on a two component support. The metal hydrogenation component is at least one of a Group VIB or Group VIII metal, preferably a Group VIII metal, and more preferably Pt or Pd. The metal is dispersed on at least one of the first and second components of the support, and preferably on both components. Typically the metal will be present in an amount ranging from about 0.1 to about 30 wt%, and preferably about 0.1 to 10 wt%. If the metal is a Group VIII noble metal, then the preferred amount is 0.1 to 5 wt%. The catalyst may also include a substantially inert binder or matrix material.

The first component is a catalytic dewaxing component including crystalline 10 and 12 ring molecular sieves. Crystalline molecular sieves include metallo-, e.g., alumino silicates, alumino phosphates and silicoalumino-phosphates. Examples of crystalline alumino silicates include zeolites, e.g., ZSM-5, ZSM-11, ZSM-12, Theta-1 (ZSM-22), ZSM-23, ZSM-35, ZSM-48 natural and synthetic ferrierites, ZSM-57, Beta Mordenite and Offretite. Examples of crystalline alumino and silicoalumino-phosphates include SAPO-11, SAPO-41, SAPO-31, MAPO-11 and MAPO-31. Preferred include ZSM-5, ZSM-22, ZSM-23, ferrierites, and SAPO-11.

The second isomerization component can be any of the typical isomerization catalyst such as those comprising amorphous refractory metal oxide support base (e.g., alumina, silica-alumina, zirconia, titania, etc.) on which has been preferably deposited a catalytically active metal selected from Group VI B, Group VII B, Group VIII metals and mixtures thereof, preferably Group VIII, more preferably noble Group VIII, most preferably Pt or Pd and optionally

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including a promoter or dopant such as halogen, phosphorus, boria, yttria, rare earth oxides, from e.g., La, Ce, etc., magnesia, etc. preferably halogen, yttria or magnesia, most preferably fluorine. The catalytically active metals are present in the range 0.1 to 5 wt%, preferably 0.1 to 3 wt%, more preferably 0.1 to 2 wt%, most preferably 0.1 to 1 wt%. The promoters and dopants are used to control the acidity of the isomerization catalyst. Thus, when the isomerization catalyst employs a base-material such as alumina, acidity is imparted to the resultant catalyst by addition of a halogen, preferably fluorine. When a halogen is used, preferably fluorine, it is present in an amount in the range 0.1 to 10 wt%, preferably 0.1 to 3 wt%, more preferably 0.1 to 2 wt%, most preferably 0.5 to 1.5 wt%. Similarly, if silica-alumina is used as the base material, acidity can be controlled by adjusting the ratio of silica to alumina or by adding a dopant such as yttria, rare earth oxides, from, e.g., La, Ce, etc., boria or magnesia which reduces the acidity of the silica-alumina base material as taught on U.S. Patent 5,254,518 (Soled, McVicker, Gates, Miseo).

The first and second components are combined in a ratio sufficient to promote wax isomerization and naphthene destruction without substantial decrease in VI. The zeolite to amorphous inorganic oxide ratios for catalysts according to the invention range from about 1:1 to 1:20 by weight, subject to the MCH test described below.

One technique for determining the proper ratio of first and second components in the catalyst is based on an evaluation of the combined components containing about 0.5 wt% Pt in converting methylcyclohexane (MCH) to various cyclopentane compounds. Catalyst that at 320°C provide a ratio of trans-1,2-dimethylcyclopentane to trans-1,3-dimethylcyclopentane (trans-1,2/trans-1,3 DMCP) in the range of at least one have been found to

promote wax isomerization and naphathene destruction of feeds without substantial decrease in VI.

The second factor is when the catalyst, impregnated with about 0.5 wt% Pt and evaluated in converting methylcyclohexane (MCH) to various cyclopentane compounds at 10% conversion, exhibits a selectivity for ethylcyclopentane (ECP) formation above at least 50%.

This technique is further explained as follows. The reaction of MCH over the catalyst to various cyclopentane products is shown in Figure 1. As indicated in Figure 1, the products of MCH decomposition include ethylcyclopentane, cis- and trans-1,2-dimethylcyclopentane, cis- and trans-1,3-dimethylcyclopentane and 1,1 dimethylcyclopentane. This technique, also known as the MCH test is used to define relative acid site concentration, strengths and active site constraint for the catalysts according to the invention.

The key factors are summarized as follows: (1) total conversion of MCH for a given catalyst weight at 320°C is an indication of the relative number of acid sites; (2) selectivity to ECP, at 10% conversion, is a measure of the relative acid strength wherein high ECP selectivity values indicates low acid strength and low ECP selectivity values indicates high acid strength; and (3) the ratio of trans-1,2-DCMP to trans-1,3-DCMP correlates with the constraint at the catalyst active site wherein a high ratio (>1) indicates little or no physical constraint at the active site and a low ratio (<1) indicates a physical constraint at the active site.

In the present process, to produce a catalyst that will give improved low temperature properties, the ratio of trans-1,2-DCMP to trans-1,3-DCMP is adjusted to from 1:1 to 2:1 predominately by controlling the acid

strength of the amorphous isomerization component. It is preferred to use higher acid strength amorphous components such as silica-alumina.

Conversely, a catalyst that will give high yield is produced by decreasing the acid strength of the amorphous phase. In this case it is preferred to use lower acid strength amorphous components such as alumina. Another way of making such a catalyst is by changing the ratio of the microporous component to the amorphous component such that the unitized catalyst has a trans-1,2 trans-1,3 DMCP ratio of less than 1.

The hydrodewaxing process utilizing the catalyst of the present invention is conducted at temperatures between about 200°C to 400°C, preferably 250°C to 380°C and most preferably 300°C to 350°C at pressures between about 500 to 5,000 psig (3.55 to 34.6 mPa), preferably 1,000 to 2000 psig (7.0 to 13.9 mPa), a hydrogen gas treat ratio of 500 to 10000 SCF H₂/B (89 to 1780 m³/m³), preferably 2,000 to 5,000 SCF H₂/B (356 to 890 m³/m³) and a LHSV of 0.5 to 5 v/v/hr, preferably 1 to 2 v/v/hr.

In an alternate embodiment of the present invention the feed is first subject to solvent dewaxing to a pour point on the order of +10°C or lower.

The dewaxing solvent used may include the C₃-C₆ ketones such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), mixtures of MEK and MIBK, aromatic hydrocarbons like toluene, mixtures of ketones and aromatics like MEK/toluene, ethers such as methyl t-butyl ethers and mixtures of same with ketones or aromatics. Similarly, liquefied, normally gaseous hydrocarbons like propane, propylene, butane, butylene, and combinations thereof may be used as the solvent. Preferably the solvent employed will be an equal

volume mixture of methyl ethyl ketone and methyl isobutyl ketone. Typically the isomerate to solvent ratio will range between 1 to 10 and preferably will be about 1:3. The dewaxed feed is then subjected to hydrodewaxing as described hereinabove.

The present invention is demonstrated below in the non-limiting examples.

EXAMPLES

Comparative Example 1

A catalyst (B) comprising 0.5 wt% Pt ZSM-5 (silica/alumina ratio 220:1) and alumina in the weight ratio of 25:75, was used in two runs to dewax a hydrocrackate distillate having the following properties:

KV, cSt at 100°C	3.808
KV, cSt at 135°C	2.28
Pour Point, °C	39
Boiling Range (GCD)	325-503°C

The dewaxing conditions employed are listed in the accompanying Table. The results are shown in column B of the Table following Example 2.

When screened for activity and selectivity with methylcyclohexane, this catalyst had an ECP selectivity of 40 and a trans-1, 2/trans-1,3 dimethylcyclopentane ratio of 0.02 as shown in the Table. A comparison of columns A and B of the Table shows that the VI of the resulting liquid product (350°C+) was lower than that obtained by solvent dewaxing. The product low temperature properties, as shown by the Brookfield Viscosity at -40°C (additized with a standard Ford type ATF adpack), are also shown in the Table. The

Brookfield Viscosity is reduced by catalytic dewaxing over that of a solvent dewaxed product. However, the Brookfield Viscosities of both solvent and cat dewaxed products are very poor.

Comparative Example 2

A catalyst (C) comprising 0.5 wt% Pt ZSM-5 (silica/alumina ratio 220:1) and silica-alumina in the weight ratio of 50:50, was used to dewax a hydrocrackate distillate having the properties noted in Comparative Example 1. This catalyst was made by combining the powdered ZSM-5 (Si/Al ratio 110) with the powdered amorphous component in the weight ratio of 50:50 and then loading platinum by incipient wetness using platinum tetraamine dichloride.

When screened for activity and selectivity with methylcyclohexane, this catalyst had an ECP selectivity of 47 and a trans-1, 2/trans-1,3 dimethylcyclopentane ratio of 0.82 as shown in the Table following Example 2. A comparison of columns A and C, in the Table shows that the VI of the resulting liquid product (350°C+) was lower than that obtained by solvent dewaxing. The product low temperature properties, as shown by the Brookfield Viscosity -40°C (additized with a standard Ford type ATF adpack), are also shown in the Table. The Brookfield Viscosity is reduced by catalytic dewaxing over that of a solvent dewaxed product but not significantly over that obtained using the alumina bound catalyst in Example 1.

Example 1

A catalyst (D) comprising 0.5 wt% Pt ZSM-5 (silica/alumina ratio 220:1) and silica alumina in the weight ratio of 10:90, was used to dewax a hydrocrackate distillate having the properties noted in Comparative Example 1. This catalyst was made by combining the powdered ZSM-5 (Si/Al ratio 110)

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with the powdered amorphous component in the weight ratio of 10:90 respectively and then loading platinum by incipient wetness using platinum tetraamine dichloride.

When screened for activity and selectivity with methylcyclohexane, this catalyst had an ECP selectivity of 50 and a trans-1,2/trans-1,3 dimethylcyclopentane ratio of 1.80 as shown in the Table following Example 2. Both of these values are within the criteria for catalysts of this invention. A comparison of columns A and D, in Table 1 shows that the VI of the resulting liquid product (350°C+) was higher than that obtained by solvent dewaxing. The product low temperature properties, as shown by the Brookfield Viscosity at -40°C (addized in a standard ECA/ATF adpack), are also shown in the Table. The Brookfield Viscosity is significantly reduced by catalytic dewaxing with this catalyst over that of a solvent dewaxed product in the Table 1.

Example 2

The procedure of Example 1 was followed using 0.5 wt% on Pt on theta-1 (TON) on silica-alumina (Catalyst E) and 0.5 wt% Pt on Al₂O₃ in the weight ratio of 25:75 (Catalyst F-Comparative). Theta-1 is a 10 ring zeolite and is described in EP 057049. This catalyst was made by combining the powdered TON zeolite (Si/Al ratio 30) with the powdered amorphous component in different ratios and then loading platinum by incipient wetness using platinum tetraamine dichloride. The condition and results are set out in columns E and F of Table 1.

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TABLE I

	A	B	C	D	E	F
Catalyst (wt%)	Solvent Dewaxing	Pt ZSM-5 (25) Alumina (75)	Pt ZSM-5 (50) Silica-Alumina (50)	Pt ZSM-5 (10) Silica-Alumina (90)	Pd TON (25) Pt Silica-Alumina (75)	Pt TON (25) Al ₂ O ₃ (75)
CONDITIONS						
Average Reactor Temperature, °C		314 329	314 329	329 339	304	314
Pressure, psig		1000	1000	1000	1000	1000
v/v/hr		1	1	1	1	1
T G Rate, scf/bbl		2500	2500	2500	2500	2500
PRODUCT PROPERTIES						
350°C+, Yield	75	72 55	65 50	55 45	75	78
Viscosity, cSt at 100°C	3.94	4.07 4.37	4.1 4.05	3.83 3.81	3.9	3.91
Viscosity, cSt at 40°C	18.56	19.48 22.41	19.528 19.84	17.33 17.306	17.663	17.713
VI	110	108 102	106 102	112 109	115	116
Pour Point, °C	-21	-14 -35	-23 -43	-20 -36	-21	-16
Brookfield Viscosity, cP at -40°C	> 25,000	18,400 22,600	18,000 16,000	12,800 12,000	12,000	17,000
MCH Conversion, at 320°C ECP trans-1,2/trans-1,3 DMCP	n/a n/a n/a	11.4 40 0.02	10.6 47 0.82	12 50 1.8	18.2 61 1.15	9.9 70 0.12

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The results shown in the Table are further illustrated in Figure 2 which is a graph showing Brookfield viscosity vs. yield for various catalyst combinations.

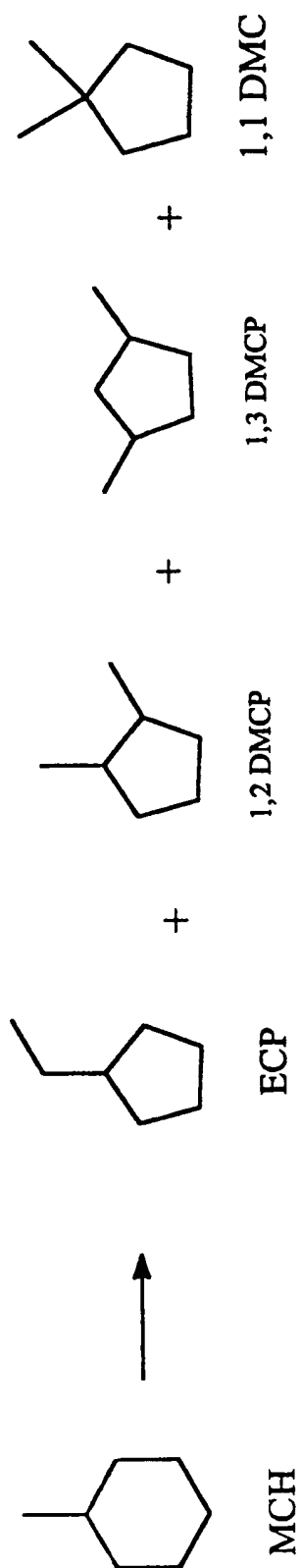
CLAIMS:

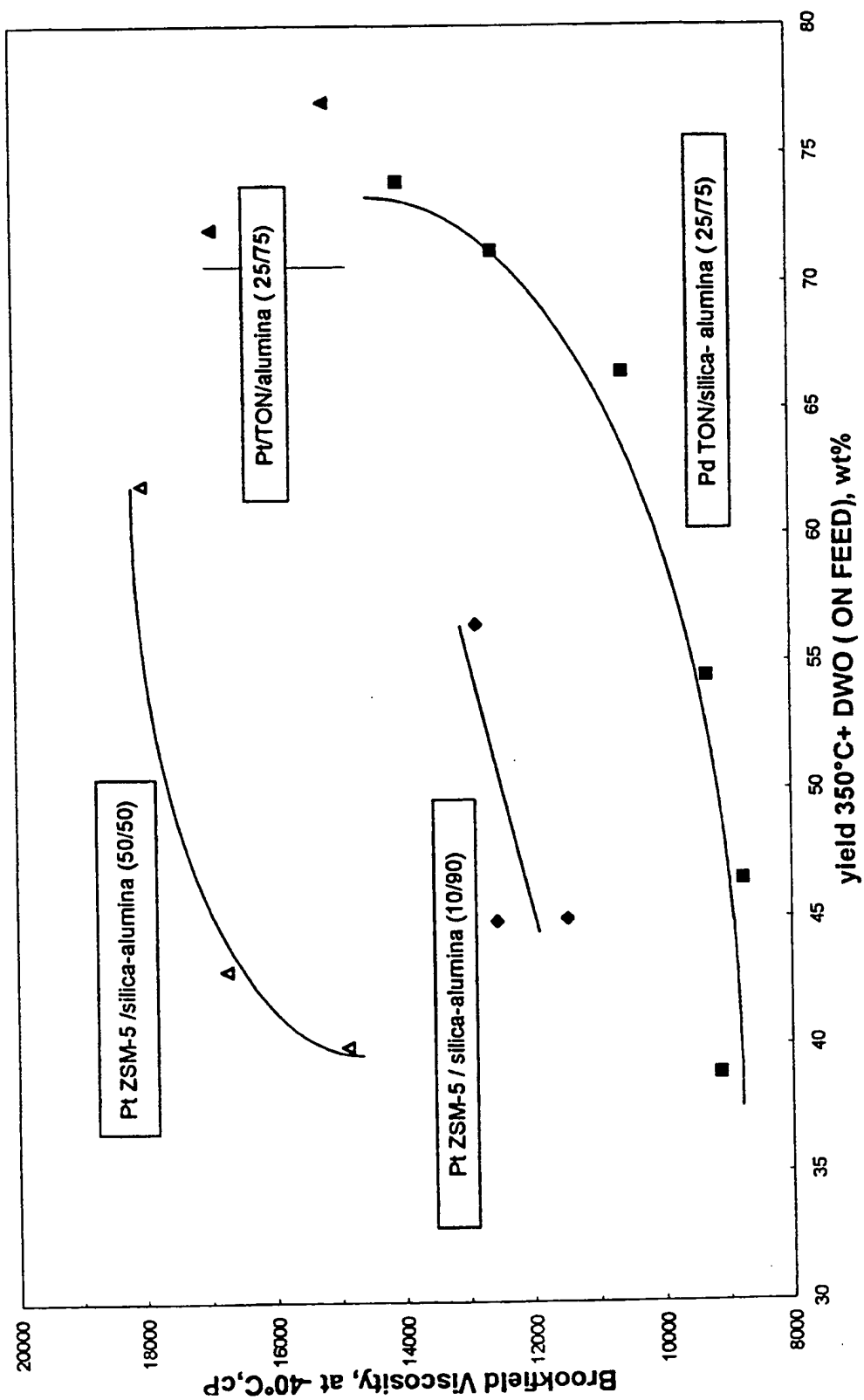
1. A method for hydrodewaxing of feeds to produce a lube base-stock having improved low temperature properties which comprises: contacting the feed with a unitized mixed powder pellet catalyst under hydrodewaxing conditions, the catalyst comprising a metal hydrogenation component on a support having a first dewaxing component and a second isomerization component, wherein the first component is selected from 10 and 12 ring molecular sieve and mixtures thereof and the second component is an amorphous inorganic oxide and wherein the first and second components are present in a ratio such that when evaluated in the conversion of methyl cyclohexane at 320°C to 1,1-dimethylcyclopentane, 1,2-dimethylcyclopentane, 1,3-dimethylcyclopentane and ethylcyclopentane, the catalyst will provide a trans-1,2-/trans-1,3-dimethylcyclopentane ratio is at least 1 and a selectivity to ethylcyclopentane, at 10% conversion, of at least about 50%.
2. The method of claim 1 wherein the metal hydrogenation component is at least one of a Group VI or Group VIII metal.
3. The method of claim 2 wherein the metal hydrogenation component is a Group VIII metal.
4. The method of claim 2 wherein the metal hydrogenation component is dispersed on at least one of the first and second components.
5. The method of claim 4 wherein the hydrogenation component is dispersed on both the first and second component.

6. The method of claim 4 or 5 wherein the hydrogenation component is dispersed in an amount ranging from about 0.1 wt% to about 30 wt%.
7. The method of claim 2 wherein in the second component when evaluated in the conversion of methylcyclohexane at 320°C will exhibit a selectivity for ECP formation of at least 50% or greater.
8. The process of claim 1 wherein the feed is a feed that is solvent dewaxed to a pour point of up to +10°C.
9. The process of claim 1 wherein the feed is hydrotreated at temperatures in the range 280°C to 400°C, at pressures in the range 500 to 3000 psi, hydrogen treat gas rate in the range of 500 to 5000 SCF/bbl and a flow velocity in the range 0.1 to 5 LHSV.
10. The process of claim 1 wherein the 10 and 12 ring molecular sieves are selected from alumino silicates and alumino phosphates.
11. The process of claim 10 wherein the alumino silicates are selected from ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, natural and synthetic ferreirites, ZSM-57, Beta Mordenite and Offretite.
12. The process of claim 10 wherein the alumino phosphates are selected from SAPO-11, SAPO-41, SAPO-31, MAPO-11 and MAPO-31.
13. The process of claim 10 wherein the molecular sieves are selected from ZSM-5, ZSM-22, ZSM-23, ferrierites and SAPO-11.

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14. The process of claim 1 wherein the amorphous inorganic oxide is promoted or doped with yttria, rare earth oxides, boria and magnesia.

FIGURE 1

**FIGURE 2**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/03006

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10G 71/00, 35/04, 35/06, 35/085, 35/095 ; C07C 5/00, 5/13, 5/22

US CL : 208/18, 134, 135, 136, 137; 585/734, 739

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/18, 134, 135, 136, 137; 585/734, 739

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: dewax?, isomerize?, ZSM?, SAPO?, molecular sieve?, ring?, amorphous

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 3,755,145 A (ORKIN) 28 August 1973 (28/08/73), see column 4, lines 46-48 and 62-63, column 5, lines 24-28, column 6, lines 34-50 and column 7, lines 24-33.	1-6, 9-11 and 13-14 ----- 8
X --- Y	US 4,960,504 A (PELLET ET AL) 02 October 1990 (02/10/90), see column 10, lines 6-19 and column 19, 32-60.	1-7 and 9-13 ----- 8
Y	US 4,181,598 A (GILLESPIE ET AL) 01 January 1980 (01/01/80), see column 3, lines 46-68 and column 4, lines 1-16.	8

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

28 APRIL 1999

Date of mailing of the international search report

13 MAY 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/03006

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,246,566 A (MILLER) 21 September 1993 (21/09/93), see column 5, lines 12-14, column 6, lines 56-68, column 10, lines 63-68 and column 13, lines 6-17.	1-14
X	US 4,259,170 A (GRAHAM ET AL) 31 March 1981 (31/03/81), see column 4, lines 36-44, column 6, lines 38-47, column 7, lines 29-45, column 8, lines 61-64 and column 10 line 68.	1-11 and 13-14
A	US 4,859,311 A (MILLER) 22 August 1989 (22/08/89), see entire document.	1-14
A	US 4,414,097 A (CHESTER ET AL) 08 November 1983 (08/11/83), see entire document.	1-11 and 13-14
X	US 4,437,975 A (GILLESPIE ET AL) 20 March 1984 (20/03/84), see column 2, lines 43-44 and 47-51, column 4, lines 3-9 and column 6, lines 43-46.	1-11 and 13-14
A,E	US 5,885,438 A (APELIAN ET AL) 23 March 1999 (23/03/99), see entire document.	1-14
A	US 5,082,986 A (MILLER) 21 January 1992 (21/01/92), see entire document.	1-14
A	US 5,139,647 A (MILLER) 18 August 1992 (18/08/92), see entire document.	1-14
A,P	US 5,723,716 A (BRANDES ET AL) 03 March 1998 (03/03/98), see entire document.	1-14
A	US 4,867,861 A (ABDO ET AL) 19 September 1989 (19/09/89), see entire document.	1-14
X	US 5,135,638 A (MILLER) 04 August 1992 (04/08/92), see column 13, lines 1-21, column 15, lines 1-11 and column 23, lines 5-10 and 36-45.	1-14